

THEORETICAL INTERPRETATION OF TAIT EQUATION PARAMETERS.*

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We have recently considered the equation of state, the cohesive energy density and the limiting internal pressure at atmospheric pressure for oligomer and polymer liquids in terms of cell theory and in relation to the principle of corresponding states.^{1,2}

Experimental isotherms at elevated pressures are well described^{3,4} by the empirical Tait equation, viz.:

$$1 - V/V_0 = C \ln (1 + p/B) \quad (1)$$

where V_0 represents the initial volume at $p = 1 \text{ bar} \approx 0$. Application of eq. (1) to hydrocarbons of varying molecular structures and weights in the lubricating range⁴ indicates that the parameter B is a function of temperature and depends on the specific system. The parameter C , on the other hand, has a universal value of 0.08936 for all the hydrocarbons investigated,⁴ independent of structure or temperature.

Some years ago, Simha and Hadden⁵ showed that the cell theory in the formulation of Prigogine et al.⁶ leads to an approximately constant value of C , whereas B should be related to the cohesive energy density. However, they used several expansions in respect to chainlength and volume ratio and found $C = 1/4$ which is too large. The purpose of this note is to clarify the relation between the Tait parameters and the theoretical equation of state. We shall make use of the square well approximation to the cell potential.² It turns out that both the constancy and the numerical value of C are accounted for quite well by the theory.

From eq. (1) there follows:

$$V_0 C = -(\partial p / \partial V)_T / (\partial^2 p / \partial V^2)_T; \quad B = (\partial p / \partial V)_T^2 / (\partial^2 p / \partial V^2)_T - p \quad (2)$$

Provided the principle of corresponding states is valid at finite pressure, eq. (2) can be cast in the reduced form:

$$\tilde{V}_0 C = -(\partial \tilde{P} / \partial \tilde{V})_{\tilde{T}} / (\partial^2 \tilde{P} / \partial \tilde{V}^2)_{\tilde{T}}; \quad B / (qze^* / V^*) = \tilde{B} = (\partial \tilde{P} / \partial \tilde{V})_{\tilde{T}}^2 / (\partial^2 \tilde{P} / \partial \tilde{V}^2)_{\tilde{T}} - \tilde{P} \quad (2a)$$

The reduced variables and the ratio qze^* / V^* are defined as previously.

Thus C must be a universal function of the reduced variables, whereas B , a characteristic pressure quantity, is specific for the system. The actual behavior of C and B can be analyzed by direct reference to the equation of state.² With eq. (2a) it yields for $\tilde{P} \rightarrow 0$:

$$C = \frac{(2^{1/6} \cdot 3)^{-1} \tilde{T} \tilde{V}^{-1/3} X^{-2} + 2 \tilde{V}^{-2} (4.044 \tilde{V}^{-2} - 2.409)}{(2^{1/6} \cdot 0.9)^{-1} \tilde{T} \tilde{V}^{-1/3} X^{-2} + (2^{1/3} \cdot 4.5)^{-1} \tilde{T} \tilde{V}^{-2/3} X^{-3} + \tilde{V}^{-2} (56.616 \tilde{V}^{-2} - 24.090)} \quad (3)$$

$$\tilde{B} / C = (2^{1/6} \cdot 3)^{-1} \tilde{T} \tilde{V}^{-1/3} X^{-2} + 2 \tilde{V}^{-2} (4.044 \tilde{V}^{-2} - 2.409)$$

Here $X = (1 - 2^{-1/6} \tilde{V}^{-1/3})$ and \tilde{V} and \tilde{T} are connected by eq. (3), ref. 2.

Fig. 1 shows C and \tilde{B} as a function of \tilde{V} or \tilde{T} . We note that

$0.104 \geq C \geq 0.090$ for $0.042 \leq \tilde{T} \leq 0.123$. This encompasses a considerably wider temperature range than the experimental range over which eq. (1) was tested.⁴ The theoretical \tilde{B} - function is also plotted in Fig. 1 and compared with the experimental \tilde{B} for n-pentadecane. The numerical value of the scale factor qze^* / V^* was chosen to give an exact fit for the experimental \tilde{B} at 44.2°C ($\tilde{V} = 1.150$) viz. 4878 bar, as compared with 4692 derived from the cohesive energy density.² A reasonable representation of the B -function thus results from the theory. We note, moreover, from the figure that the limiting compressibility C/B is about 10% higher than is observed for n-C₁₅ in the region of validity of the theory, $\tilde{V} < 1.20$.²

Similar comparisons of the Tait parameters at elevated pressures could be carried out. This would be equivalent to a comparison of experimental and theoretical isotherms at elevated pressures. Such a comparison was actually

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made for n-pentadecane and n-octadecane below 100°C , the region in which simple cell theory is applicable to these compounds.² A satisfactory representation of the experimental data up to about 700 bars is possible. However the numerical value of the pressure parameter qze^*/V^* required is about 16% higher than that derived above from the temperature dependence of B . A variation of the parameters in the interpretation of different properties by means of an approximate theory is to be expected. However, a fuller discussion of the equation of state at elevated pressures is preferably postponed, until a better representation of internal pressure and compressibility² at low pressures is achieved.

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¹R. Simha and A. J. Havlik, J. Am. Chem. Soc. 86, 197 (1964).

²V. S. Nanda and R. Simha, submitted for publication.

³R. E. Gibson and O. H. Loeffler, Ann. N. Y. Acad. Sci. 51, 727 (1949).

⁴Cutler, McMickle, Webb and Schiessler, J. Chem. Phys. 29, 727 (1958).

⁵R. Simha and S. T. Hadden, J. Chem. Phys. 25, 702 (1956).

⁶I. Prigogine, N. Trappeniers, and V. Mathot, Disc. Farad. Soc. 15, 93 (1953).

Legend for Figure

Fig. 1. Variation of Tait parameters with reduced volume or temperature at atmospheric pressure. Dashed line C, experimental. Δ Experimental \tilde{B} for n- C_{15} , temperature range $38 - 120^{\circ}\text{C}$. Bars indicate high temperature limit of theory.²

